PRODUCTION OF MEMBRANE FOR CO_2/N_2SEPARATION EFFECT OF DILUENTS EXTRACTION TIME ON PP-DPE MEMBRANE

AHMAD FADHIL HANAFI BIN ABDULLAH

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

ABSTRACT

The main factors that contribute for the raising of global warming are CO_2 gas. Production of membrane is actually one of the methods for the separation of CO_2 gas. Membrane technology is continuity and simplicity process compared to the others conventional separation technology. The membranes were prepared from thermal induced phase separation method with 80 wt% of diphenyl ether using the hot steel as a casting with thickness of 500 µm. The membranes were selected to extract into the methanol within 1 hour, 2 hours, 3 hours, and 4 hours of immersion. For the physical and chemical characterization membrane, Scanning Electron Microscopy (SEM) and Fourier Transform Radiation (FTIR) will be used. This research need to calculate the gas permeability and selectivity after single gas permeation is tested with different of pressure. Refer to SEM analysis, the figure for the 4 hours time diluents extraction gives the better pore production compare to 3 hours, 2 hours and 1 hour diluents extraction as the methanol completely remove all the air inside the membrane. If the methanol completely removed the air inside the membrane, the image capture becomes clear and better pore will produced. For FTIR analysis, there have no different functional group inside the membrane after immersed into the methanol. From 1 hour until 4 hours of diluents extraction of membrane have the same functional group of alcohol with the structure of (O-H) stretch that mean the presence of methanol inside the membrane and functional group of ether (C-O-C) stretch and alkanes (C-H) stretch since the membrane is produced by polypropylene and diphenyl ether as a solvent. For the gas permeation, the diluents extraction into methanol for 4 hours gives the highest permeability for the CO_2 and N_2 single gas permeation test. The relation between gas permeation tests with SEM morphology test for the better pore on cross section membrane will cause the good permeability on CO_2/N_2 gas. However, it is difficult to ensure the selectivity of the membrane increase when the permeability increase since the permeability is inversely proportional to selectivity.

Keywords: Polypropylene membrane; methanol immersion; diphenyl ether; gas permeation

ABSTRAK

Faktor utama yang menyumbang kepada peningkatan pemanasan bumi adalah berpunca daripada gas CO_2. Penghasilan membran adalah salah satu cara untuk memisahkan gas CO_2. Teknologi penghasilan membran adalah proses yg lebih mudah berbanding teknologi proses pemisahanan yang lain. Membran telah dihasilkan melalui proses therma pemisahan fasa dengan kepekatan 80 wt% eter diphenyl dengan menggunakan besi panas sebagai alat pemutus dengan ketebalan 500 µm. Membran telah dipilih untuk direndam kedalam methanol selama 1 jam, 2 jam, 3 jam dan 4 jam masa rendaman. Untuk menguji sifat fizikal dan sifat kimia membran, pengimbasan electron mikroskop (SEM) dan fourier transform spectroskopi inframerah (FTIR) akan digunakan. Kajian ini perlu mengira kebolehtelapan dan pemilihan selepas penyerapan gas tunggal diuji dengan perbezaan tekanan. Merujuk kepada SEM, gambar yang mempunyai masa rendaman selama 4 jam mempunyai liang yang lebih baik berbanding 3 jam, 2 jam dan 1 jam rendaman pengekstrakan bahan pencair kerana metanol telah mengeluarkan kesemua udara di dalam membran. Untuk FTIR analisis, tiada perbezaan antara kumpulan berfungsi di dalam membran selepas direndam kedalam metanol. Dari 1 jam hingga 4 jam rendaman, membran mengandungi kumpulan berfungsi seperti alkohol dengan struktur (O-H) regangan membuktikan kewujudan metanol di dalam membran, kumpulan berfungsi seperti eter (C-O-C) regangan dan alkana (C-H) regangan kerana membran diperbuat daripada polipropilena dan diphenyl eter sebagai bahan pencair. Untuk kebolehtelapan gas, rendaman kedalam metanol selama 4 jam menghasilkan kebolehtelapan yang paling tinggi untuk gas CO_2 dan N_2. Bagaimanapun, amatlah sukar untuk memastikan pemilihan membran meningkat apabila kebolehtelapan meningkat kerana hubungan antara mereka adalah berkadar songsang antara satu sama lain.

Kata kunci: membran polipropilena; metanol rendaman; Diphenyl eter; gas penyerapan

.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

α	Selectivity
Δp	Pressure different across membrane

LIST OF ABBREVIATIONS

PP	Polypropylene
CO_2	Carbon Dioxide
N_2	Nitrogen
CH_3OH	Methanol
DPE	Diphenyl Ether
SEM	Scanning Electron Microscope
FTIR	The Fourier Transform Infrared Spectroscopy
TIPS	Thermally Induced Phase Separation
PA	Permeability of desired gas (CO_2)
PB	Permeability of desired gas (CH_4)
Pi	Permeability coefficient of gas
Qi	Volumetric flowrate of gas i
A	Membrane effective surface area
l	Membrane skin thickness
(p/l)i	Pressure normalize flux or permeability of gas i
Q	Permeate volumetric rate

1 INTRODUCTION

1.1 Background

In our life, carbon dioxide gas already release to the surrounding naturally. At the same time, many industrial remove the CO_2 gas as a waste product. As a result, the composition of CO_2 in the air will be increase. Unfortunately, this CO_2 gas is not good for human health. Back to the origin, CO_2 gas is a chemical compound of two oxygen atoms that have a covalent bond with a single carbon atom. As a gas, CO_2 is colorless and odorless that is harmful to human health in a concentration higher than 5000 ppm. The first person to discover CO_2 in gas form was Flemish Chemist Jan Baptist Van Helmond in the 17^{th} century, and the properties of CO_2 were further researched by Scottish physician Joseph Black in the 18^{th} century (Clem et al., 2006).

One of the effects that were created by CO_2 gas is the global warming and has been identified as the world's major environmental issues. This problem is made from the greenhouse effect. Actually, the greenhouse's function is to warm the earth by trapping the CO_2 gas inside the atmospheric layer. According to the increasing of CO_2 gas composition in the air that are release from the industries, the greenhouse gives the negative impact for the earth because it trapped too many CO_2 gas inside the atmospheric layer. As a result, the earth's temperature will be increase. Besides that, the increasing of the earth temperature also gives a side effect such as snow melt in the arctic, rise of sea level and shrinking the size of an area of the land (Nomura et al., 2010).

In order to separate this CO_2 gas, there are various types of CO_2 gas removal process such as solvent absorption, solid adsorption, direct conversion, cryogenic fractionators and membranes. This research will focus on membrane separation process. Membrane technology is continuity and simplicity process compared to conventional separation technology. Besides, this technology is flexibility in designed because it can be combined with each other and with other separation technologies to meet complex demand in separation technology. The other characteristic of membrane technologies

that give significant advantages to the industries is the compactness of it design that suitable for the plant that limited in area (Baker, 2002).

Polymer is the substances that can be used to prepare the membrane. In order to produce the membrane, it is important to select the suitable types of polymer. polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE) and polyvinylchloride (PVC) are an example of the polymer that are suitable to produce the membrane. This research will select the PP for the membrane production. The advantages of choosing PP rather than other polymers is because PP is a plastic material known for its ability to withstand very high temperatures without warping, its general sturdiness, and its water resistance. Normally, CO_2 gas release from the chemical plant in a high temperature. So, it is relevant to choose polypropylene as a material to produces the membrane.

1.2 Problem statement

Separation of CO_2 is one of the important processes in many industrial areas. Membrane gas separation was chose as a CO_2 capture technique. As we know, the main problems is the used of membrane based separation process in a wide range of application is the lack of membrane with high selectivity and permeability. Usually, membrane with high selectivity gravitate to exhibit less permeability. It is difficult to search the membrane with high selectivity and permeability at the same time as the selectivity is inversely proportional to the permeability. It is important to select the most compatible combination of polymer and solvent formulation to get the best performance of the membrane. The diluents extraction time of the membrane into the methanol is one of the significant factors in determining the membrane performance. The methanol actually can be used as an agent to remove the air inside the membrane. When the air inside the membrane is removed, the pore can be produced easily. Therefore, membrane formation based on the formation of the pore is an important part to get a good membrane performance for gas separation.

1.3 Objective

To study the performance of produced polypropylene membrane using gas separation.

1.4 Scope

1. Preparation of membrane using TIPS method from polypropylene and diphenyl ether with percentage 80 wt% of polypropylene with four different times of diluents extraction of membrane into methanol (1 hour, 2 hours, 3 hours and 4 hours times of immersion).
2. Physical and chemical properties of produced membrane are characterized using SEM and FTIR.
3. Test for CO_2/N_2 gas separation using single gas permeation set in FKKSA lab.

2 LITERATURE REVIEW

2.1 Membrane Separation Process

There are many uses of membranes in the industries such as ultrafiltration, reverse osmosis, gas separation and many more. Table 2.1 shows that approximate data for commercialization of membrane technology for various applications according to the year (Perez and Zhang, 1997).

Table 2-1: Commercialization of the membrane technology for various applications according to the year

Technology	Industrial application	Commercialization
Electrodialysis	Desalination of bracklish water	1952
Reverse Osmosis	Desalination of bracklish seawater	1965
Ultra	Paint recovery (electrocoat)	1965
Electrosynthesis	Chlorine/caustic production	1972
Gas separation	Hydrogen recovery	1979
Pervaporation	Alcohol removal from water	1979
Nanofiltration	Softening of hard water	1990
Microfiltration	Filtration of portable water	1994

2.1.1 Ultrafitration

Ultrafiltration is one of the processes that attribute on the separating of small particles and diffuse molecules from fluids. Ultrafilters are the process of removing or rearrangement of sugars, non aqueous solvents, the separation of free from protein-

bound ligands, the elimination of materials of low molecular weight, of the rapid change of ionic or pH environment (Munir, 2006). The factor that can affect the separation process is the molecular size of the molecule. If the molecules have the same molecular size, the process cannot be removed. From the theory, the smaller pore size of the molecules will pass through the filter while the bigger molecules are sustained by the filter then it will be concentrated. The amplitude of material from 1K to 1000K (MW) is contains by certain ultrafiltration membrane, while salt and water will pass through (Maatsura, 1996).

2.1.2 Reverse osmosis

Reverse osmosis is the process where the salts and smalls molecules from lower molecular weight solutes are separated at high pressure (hydrostatic pressure). Usually, reverse osmosis rated by reservation of sodium chloride. The main function of the reverse osmosis is used to purify tap water to purities that excel distilled water quality. Figure 2.1 show the reverse osmosis process.

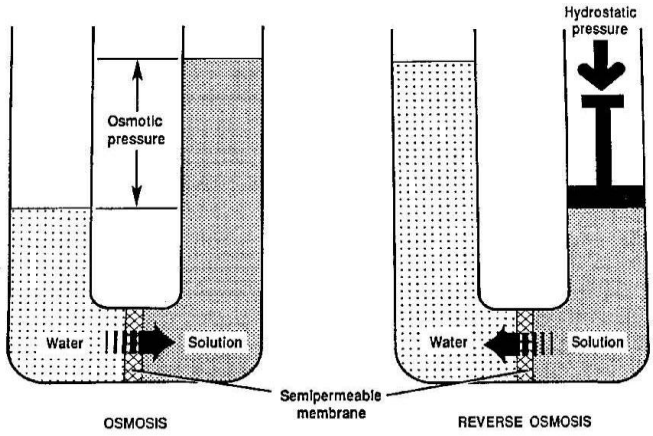

Figure 2-1: Reverse osmosis process

2.1.3 Gas Separation

Membrane gas separation normally used hydrostatic pressure and concentration gradient as a driving force. There are many applications of the membrane gas separation especially for the hydrogen gas mixture. Hydrogen recovery for synthesis gas ration

adjustment for H_2/CO_2 gas, H_2 recovery from hydroprocessing purge stream and H_2 recovery from ammonia plant purge streams and other petrochemical plant stream. Other than that, it also can be used to separate oxygen/nitrogen mixtures, recovery for helium gas and biogas processing (Scott, 1998).). Table 2.2 below shows application of membrane gas separation units.

Table 2-2: Application of membrane gas separation units (Nunes and Peinemann, 2006)

Gas Separation	**Application**
O_2/N_2	Nitrogen generation Oxygen enrichments
H_2/hydrocarbon	Refinery hydrogen recovery
H_2/CO	Syngas ration adjustment
H_2/N_2	Ammonia purge gas
CO_2/CH_4	Acid gas treating enchanced oil recovery landfill gas upgrading
H_2S/hydrocarbon	Sour gas treating
H_2O/hydrocarbon	Natural gas dehydration
H_2O/air	Air dehydration
Hydrocarbon/air	Pollution control hydrogen recovery
Hydrocarbon from process streams	Organic solvent recovery monomer recovery

2.1.3.1 History of membrane in gas separation system

In 1829, Thomas Graham found the gaseous osmosis for the air carbon dioxide system through a wet animal bladder. (Kesting and Fritzsche,1993). After that, in 1831 J.K. Mitchell noted that CO_2 gas was observed by rubber film to a larger degree than other gases, and was led to infer, accordingly, noticed that rubber expand with volume hence porosity was induced in solid sample which provide awa of penetration of CO_2 molecules. Then, 1866 Graham's law of diffusion was found. He describe about "sorption diffusion" theory of gas transport through membrane. In his researched, gas is permeated through a film (natural rubber) into vacuum not into air. He set up a series of relative permeation rates across the film for a number of gases that is amazing lose to modern estimates of the corresponding properties then state that no relation between these values and known diffusion coefficients in gases. Graham then, test for the first membrane gas separations and acquire oxygen riched air containing 46.6% oxygen. He discover that changes in the thickness of films affects the flux but not the composition of permeate gas. On 1891, Kayser show the validity of Hendry's law for adsorption of CO_2 in natural rubber (Raul and Yampol' ski, 1994). The information and knowledge about the gas separation in membrane continues discovered until nowadays.

2.1.3.2 Absorption

Absorption application was found to remove the acid gas such as carbon dioxide and hydrogen sulphide (Maclean et al, 1986). This process actually is a physical process where a gas selectively diffused in a liquid and subsequently recovered through the effect of heat, pressure or chemical. The absorption take place when normal boiling point of component operated or one or more of component have strong affinity for a particular solvent. One of the examples the application of absorption is CO_2 removal for synthesis gas and for scrubbing CO_2 and sulphur compound from natural gas.

2.1.3.3 Adsorption

Adsorption process apply the technique porous solid such as zeolite, carbon molecular sieve and aluminosilicates material to prefer adsorb one gaseous species versus others. The adsorbent is packed in carbon steel vessels and a higher pressure is used to adsorb while a lower pressure is used to desorb.

2.1.3.4 Membrane

Membrane is a thin barrier between feed and permeate gas stream and had been used to carry fluids. Thin asymmetric membranes was first assembly which contain of a thin, dense, outside layer was formed on a porous base layer, thick and developed from cellulose acetate (Loeb and Sourirajan, 1963). Gas separation is used to separate the mixture of gases using porous or non- porous membrane. This mechanism is quite different of transport involved. Separation of porous membrane is through the difference in Knudsen flows of component in the pores which are less size than mean free path of the molecules. Meanwhile, separation of gas through non-porous depend on different in permeability's of gases.

2.1.3.5 Comparison between gas separation

Summary of the gas separation system with their performance as shown in Table 2.3

Table 2-3: Comparison of Gas Separation Systems

Process	Advantages	Disadvantages
Cryogenic Distillation	• Low power consumption • Could produce high purity products. • Could achieve higher recovery compared to other process.	• Unable to economically scale down to very small size. • Consist of highly integrated, enclosed system which does not permit easy handling of widely varying feed streams.
Adsorption	• Could obtain high purity of products. • Can be supplied to remote locations where equipment size is critical.	• Lower recovery of products. •Single relatively pure product.

Absorption	• Excellent for CO2 and H2S Removal	• High partial pressure needed for physical solvents • Low partial pressure needed for chemical solvent slow purity of acid gas
Membrane	• Versatility • Simplicity • Stable at high pressure • Could achieve high purity of product.	• Possible recompression of permeate. • Medium purity.

2.2 Membrane Module

Membranes actually need a module for large surface area. Many types of module are used in the industries such as plate and frame module, tubular module, hollow fiber module and flat sheet module. There are many type of membrane that can be used as a good separator such as flat sheet into spirally wound modules or bundles of hollow fibers and casting epoxy resins on both ends and then encasing the bundle in carbon steel shells with appropriate entrance and exit nozzles (Maclean et al, 1986).

2.2.1 Plate and Frame

Plate and frame module is the uncomplicated module's structure and not arrogation for membrane replacement. This module has its own advantages such as low volume hold up per unit membrane area and ability to process highly viscous solution because of thin channel height (0.3-0.6 mm) (Belfort, 1988). This plate support a configuration which is closest to the plate membranes used in laboratory. The skills to apply this module firstly, sets of the two membranes are placed in a sandwich like with their feed sides facing each other, in each feed and permeate compartment thus obtained a suitable spacer is placed. The number of sets needed for a given membranes are furnished with sealings rings and the two end plates then builds up to a plate and frame stack.

2.2.2 Tubular

This module process need a number of membranes of tubular shape are closed in a container. The feed will flow through the center of the tubes while the permeate flow through the porous supporting tube into the module housing. Tubular module configuration commonly introduced by ceramic membrane. Energy consumption increases to per unit amount of liquid. Unfortunately, this module cannot operate by itself and need to be supported by a tube from outside.

2.2.3 Hollow Fiber

This module contains of a large number of fibers join together in a module. The self supporting membrane is suitable to use in this module. There are two arrangement of this module firstly, inside out where the feed solution passes through the bore of the fiber and the permeated is collected on the outside of the fiber. Secondly, outside in where the feed solution enters the module on the shell side of the fibers and the permeated passes into the fiber bore. Common diameters of hollow fibers are 25-200 μm. Since no breaks or defects are allowed in a module, this requires very high standards of reproducibility and quality controls (Baker et al., 1991).

2.2.4 Flat Sheet

The flat sheet membrane is different among others because it is a simplest membrane module and easy for replacement. It is easy to prepare, handle and mount. Two membranes are placed in a sandwich-like fashion with feed side was feed each other (Teo et al., 2008). Figure 2.2 shows the flat sheet membrane.

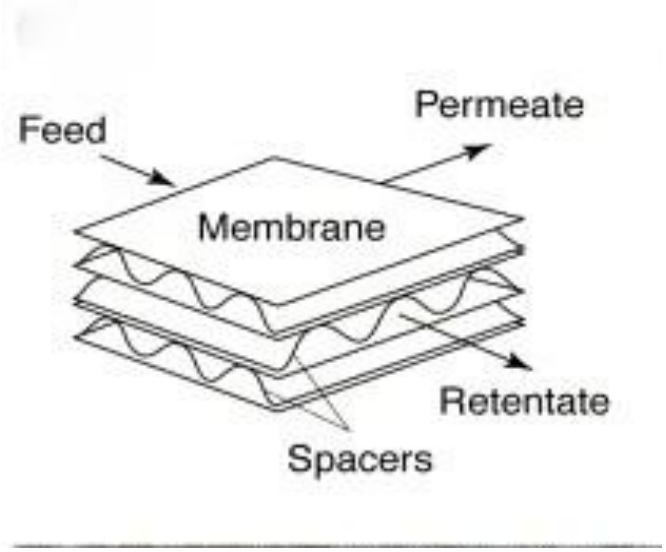

Figure 2-2: flat sheet module

2.3 Membrane Classification

There have a few sample of membrane listed that had been found but most of them still have the similar main principle and configuration.

2.3.1 Microporous Membrane

Membrane react nearly such a fiber filter and separates by a sieving mechanism detected by the pore diameter and particle size. Substances such as ceramics,graphite, metal oxide and polymers were used in making such membranes (Scott et al.,1998).

2.3.2 Electrically Charged Membrane

An ion changing membranes consist of highly swollen gels conducting a fixed positive or negative charges. These are generally used in the electro dialysis**.**(Nunes *et al.*, 2003)

2.3.3 Assymmetric Membrane

Asymmetric membranes are consumed primarily for pressure driven membrane processes, such as ultrafiltration and gas separation. Their structure consist of a very thin (0.1 to 2.0μm) polymer layer on highly porous 100 to 200μm thick sublayer (Strathmann, 1986). The sublayer only acts as a support and does not affect the separation characteristics or the permeation rate of the membrane in pressure driven processes. To obtain high permeation rates, the selective layer of gas separation membranes must be extremely thin (Baker, 2002). The advantage of asymmetric membranes is the membranes are surface filters retaining all the rejected materials at the surface where they can be release by shear forces applied by the feed solution moving parallel to the membranes surface (Costello, 1994)

2.4 Method to Produce the Membrane

2.4.1 Phase Inversion

This process is a casting solution consisting of polymer and solvent is immersed into a non-solvent coagulation bath. The mixtures then dissolved causes the casting solution will go through a phase transition by which the membrane then formed. The phase inversion process involves two different types of phase transition which is liquid-liquid phase, two-phase region and solidification phase (Pinnau 1991). There are many type of phase inversion method such as thermal precipitation, air casting of dope solution, precipitation from the vapor and immersion precipitation.

2.4.1.1 Immersion Precipitation

Immersion precipitation casting of a polymer as a thin film on a support or extruded through a die, and is subsequently immersed in a non-solvent bath. Precipitation can occur because of the good solvent in the polymer solution is exchanged with non-solvent in the coagulation bath (Fleming, 1998).

2.4.1.2 Air Casting of Dope Solution

Air casting technique process used the polymer to dissolve in a mixture of a volatile solvent and less volatile non solvent. During the evaporation of the solvent, the solubility of the polymer decreases and then phase separation will occur.

2.4.2 Thermal Phase Induce Separation

Membrane preparation using thermal induce phase separation (TIPS) is the preparation of membrane includes phase separation of polymers. In the late 1970s and early 1980s, TIPS was assembly by Castro and then patented by several people for the preparation of microporous polymeric membranes and used by various companies (Chen et al., 2009). The advantage of TIPS is suitable for wide applications for semi-crystalline polymer. On the other hand, the process is flexible, good mechanical properties, thermal stability, chemical resistance and low cost. TIPS method is operate to formed pore in the membrane layer. One efficient way to control pore size in the layer by cooling both side of the uniform solution. Using TIPS the polymer must be mix with diluents. After that, the membrane will produced and started to be characterized and tested its performance.

3 METHODOLOGY

3.1 Research Design

Figure 3.1 shows the flowchart of the workflow in this research.

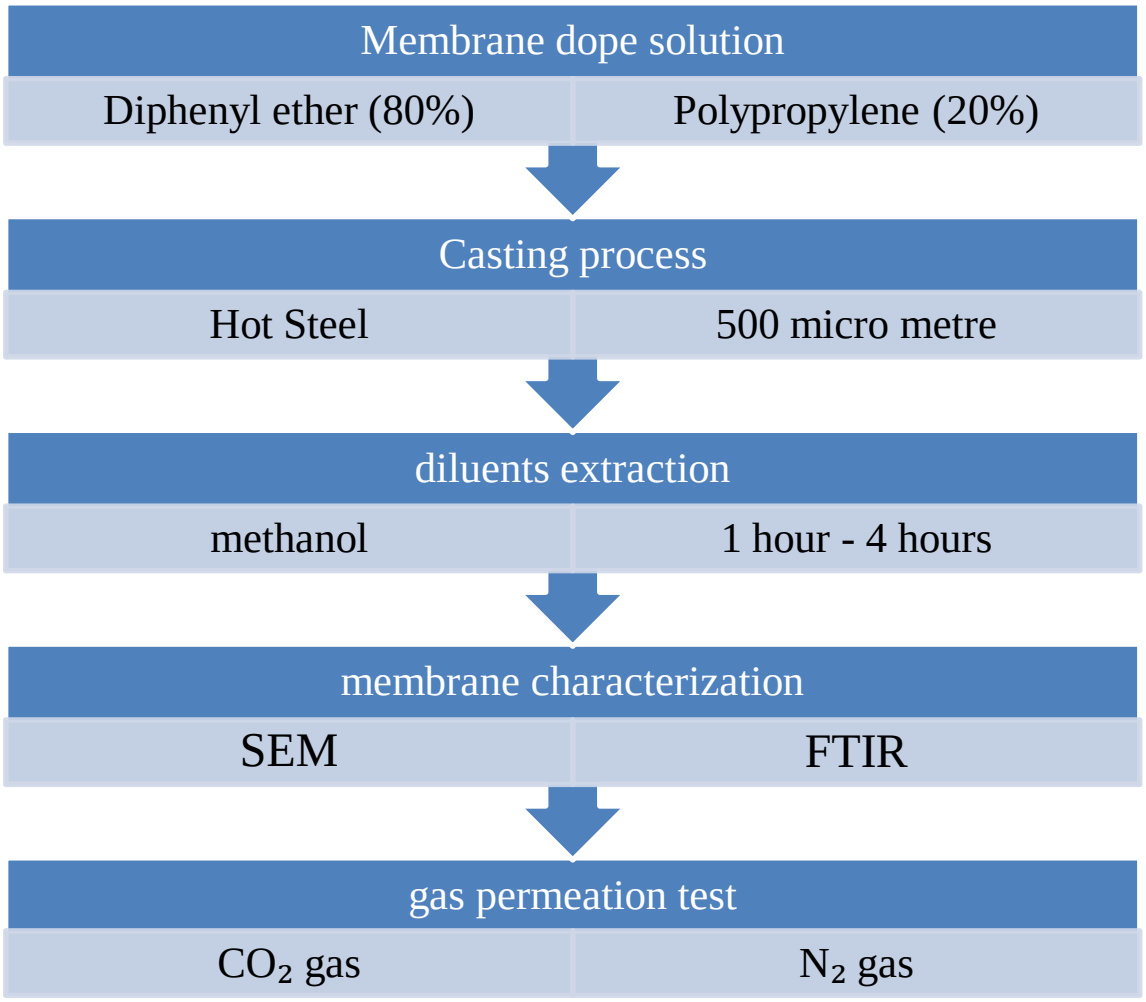

Figure 3-1: the flowchart of the workflow

3.2 Material Selection

3.2.1 Isotactic Polypropylene (iPP)

Isotactic Polypropylene (iPP) from Sigma Aldrich was used in this experiment. Figure 3.2 below shows the chemical structure of iPP.

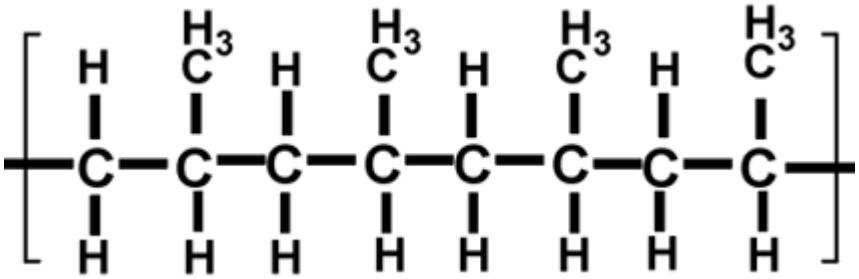

Figure 3-2: the chemical structure of iPP

Table 3-1: basic Properties of (iPP).

Properties	**Values**
Melt index	12g/10min(230°C/2.16kg)
Mol wt(g/mol)	Average Mw= 250 000
Hardness	100 (Rockwell R, ASTM D 785-A)
Transition Temperature (°C)	160-165
Density (g/mL)	0.9
Melting Point (°C)	160-166